(12) PATENT ABRIDGMENT **(11)** Document No. **AU-B-56401/86**
(19) AUSTRALIAN PATENT OFFICE **(10)** Acceptance No. **589172**

(54) Title
ACRYLATE RESIN BASED ADHESIVE COMPOSITIONS AND THEIR USE FOR ANCHORING

(51) International Patent Classification(s)
C09J 003/16

(21) Application No. : 56401/86 (22) Application Date : 16.04.86

(30) Priority Data

(31) Number	(32) Date	(33) Country
3514031	18.04.85	DE FEDERAL REPUBLIC OF GERMANY

(43) Publication Date : 23.10.86

(44) Publication Date of Accepted Application : 05.10.89

(71) Applicant(s)
HILTI AKTIENGESELLSCHAFT

(72) Inventor(s)
LUDWIG GEBAUR; PETER MAUTHE; Dr. Ing. GUSZTAV LANG

(74) Attorney or Agent
SHELSTON WATERS

(56) Prior Art Documents
GB 2058451

(57) Claim

1. An acrylate based radically hardenable adhesive, bonding and sealing composition comprising a hardenable acrylate being the reaction product of a first reactant and a second reactant, said first reactant being acrylic acid or an acrylic acid derivative and said second reactant being bisphenol, a Novolak compound containing an epoxy group, or a combination thereof.

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FORM 10

PATENTS ACT 1952

COMPLETE SPECIFICATION

FOR OFFICE USE:

Class Int.Class

Application Number: 56401/86.
Lodged:

Complete Specification Lodged:
Accepted:
Published:

This document contains the amendments made under Section 49 and is correct for printing.

Priority:

Related Art:

Name of Applicant: HILTI AKTIENGESELLSCHAFT

Address of Applicant: SCHANN, LIECHTENSTEIN

Actual Inventor: LUDWIG GEBAUR, PETER MAUTHE AND DR. ING. GUSZTAV LANG.

Address for Service: SHELSTON WATERS, 55 Clarence Street, Sydney

Complete Specification for the Invention entitled:

~~"ADHESIVE AGENTS ON AN~~ "ACRYLATE RESIN BASED ADHESIVE COMPOSITIONS AND THEIR USE FOR ANCHORING"

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

This invention relates to acrylate resin based adhesive compositions and their use for anchoring.

Adhesive and bonding compositions based on reactive resin materials such as unsaturated polyester resins, polyurethanes or formation partners thereof, have been known for a long time. Typically, a two-component system is involved. The first component includes the reactive resin, that is a reaction partner, and the second component the hardener or the other reaction partner. Other components such as fillers, activators, stabilizers, solvents, including reactive solvents, pigments, etc. may be contained in either one and/or the other component. The reaction whereby a hardened product is formed is initiated by mixing the two components.

For fastening anchor rods in drill holes, cartridges which contain two chambers for separating the components of the cartridge are generally used. The cartridge is placed into the drill hole and by rotating the inserted anchor rod in the drill hole, the cartridge and the two chambers are destroyed, thereby mixing the two components. The hardened reactive resin material enables an equal load distribution over the support area. This type of anchor has proved its value in the past, especially for heavy duty anchoring.

However, prior art adhesive compositions suffer from several inherent disadvantages. For example, adhesive compositions based on unsaturated polyester resin systems produced from dialcohols or dicarbonic acids such as o-

and/or isophthalic acid, maleic or fumaric acid have certain weaknesses due to increased demands on adhesiveness and on bonding. These systems are limited as to their thermo-forming resistance (thermo-forming resistance according to Martens 50 - 70°C) and their ageing resistance, especially under the influence of humidity, temperature changes and alkalinity.

On the other hand, polyurethane systems undergo strong secondary reactions, in the presence of humidity. Apart from the normal reaction between polyol and isocyanate, a competitive reaction with water occurs. Since the water-isocyanate-reaction proceeds more quickly, a part of the isocyanate is uncontrollably lost when CO_2 is formed for the polyurethane formation. Accordingly, structural faults are unavoidable.

An object of the present invention is to provide adhesive compositions which avoid or ameliorate the disadvantages of the prior art. It is a further object of the invention to provide adhesive compositions having additional advantages over the prior art as described hereunder by way of example.

According to one aspect, this invention consists in an acrylate based radically hardenable adhesive, bonding and sealing composition comprising a hardenable acrylate being the reaction product of a first reactant and a second reactant, said first reactant being acrylic acid or an acrylic acid derivative and said second reactant being bisphenol, a Novolak compound containing an epoxy group, or a combination thereof.

The invention is based on this recognition that the monomer or oligomer reaction compounds provide specific advantages due to the reaction described above.

Preference is given to derivatives of bisphenol A or F and of Novolak compounds. It is highly preferred that these compounds have a benzyl group content of 3 to 8.

Desirably, the bisphenol and Novolak compounds for use in the present invention include mono- and diepoxides of diphenylmethane although diepoxides are preferred. Oligomer polybenzyl derivatives are also suitable.

Acrylic acid derivative compounds having a free carbonic acid group or a functional carbonic acid derivative which reacts with epoxides are also suitable for use in the invention. Preferably, acrylic acid per se, meth-acrylic acid derivatives and acid derivatives of these two compounds, e.g. esters, amides or halogenides, especially their chlorides and derivatives, e.g. -halogen or other lower alkyl substituted derivatives are used. Desirably, the esters have an aliphatic chain, preferably an aliphatic alcohol having from 1 to 5 carbon atoms. However, phenol and cyclo-hexanol substituted esters are also suitable for use in the present invention.

Especially useful are reaction products formed by the reaction of acrylic acids and their derivatives with bisphenols containing two epoxy groups and/or with Novolaks which contain one epoxy group per phenol nucleus. Preferably, the epoxy residues are combined with the bisphenols and/or Novolaks via an ether bond, although

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a direct C-C bonding is not excluded. The ether bridge directly attaches to the phenol nucleus, i.e. the epoxy compounds are combined with the phenol nucleus under the influence of etherization of the phenolic OH groups.

Preferably, the epoxy groups are epoxy-alkyl residues which are combined with the bisphenols and/or Novolaks via, for example, an ether bridge or in another manner. These epoxy-alkyl groups have, in a direct chain, 2 - 5 carbon atoms and preferably 3 - 4 carbon atoms. Special preference is given to epoxy-bisphenols and/or epoxy-Novolaks which have an epoxy group at the end of their chain. Suitable examples are bispropoxy-bisphenols and monopropoxy-Novolaks with epoxy groups at their chain end, whereby the propoxy group is combined with the nucleus, directly via the ether-oxygen bridge.

The epoxy-acrylate resin contained in the adhesive, bonding and sealing compositions in accordance with the invention preferably has a molecular weight of less than 1500 and more preferably less than 1200. However, higher molecular weight compounds e.g. up to 2000 or above, are not excluded. Reactive resins contained in the invention-specific compositions are explained by means of prototypes depicted in Figures 1 and 2. They may be produced in the manner depicted in Figure 3.

Reactive resins, as described, which have been derived from the bisphenolic type, and may also be contained in a mixture with Novolak types, have proved successful, whereby the content of the Novolak type derived reactive resins may amount to 60% and especially to 30% in relation to the total weight of the two previously mentioned reactive resins.

Radically hardenable reactive resins may be hardened by initiators such as diaryl-peroxides, e.g. dibenzoyl-peroxide (BP) or bis(4-chlorbenzoyl)peroxide (CLBP), ketone peroxide, e.g. methyl-ethyl-ketone-peroxide (MEKP) or cyclo-hexanone-peroxide (CHP), alkyl-perester, e.g. t-butyl-perbenzoate (TBPB) etc. Hardeners are contained in their usual amounts, e.g. between 0.5 and 5 percent by weight of the total mass.

These initiators may be used in their pure form (e.g. TBPB) or phlegmatized (e.g. with gypsum, chalk, phthalate, chloro-paraffine, water) as powder, emulsion or paste. Additives, such as fillers, may be included. Reinforcing fillers include quartz, glass, corundum, porcelain, earthenware, baritem, chalk, etc., and may be added to the resin solution and/or the hardener (initiator) in the form of sands, powders or specially shaped bodies (cylinders, spheres, etc).

The bisphenol-A-acrylates and -methacrylates, as well as the bisphenol-F-acrylates and -methacrylates have, for example, molecular weights in the range of 450 to 800, whereas the Novolak acrylates and -methacrylates, depending on the number of phenol nuclei, e.g. three to eight of the starting Novolak epoxides, have molecular weights in the range of 780 to 2000.

Reactive thinners are not essential. They may, however, be used to achieve the desired viscosity. As reactive thinners the appropriate compounds, e.g. monostyrol, divinyl-benzol, alkyl-ester of polybasic acids, methacrylic acid methyl ester, methacrylic acid-i-propylester, methacrylic acid-i-butyl ester and similar, may be used.

The resin solutions may be preactivated with activators which are usually employed for cold hardening, unsaturated polyester resins. Such activators are, for example, dimethyl aniline, diethyl aniline, dimethyl-p-toluidine, cobalt octoate, cobalt naphthenate, as well as cobalt/amine activator mixtures.

It will be apparent that the compositions of the present invention offer the following advantages:

(a) the positive advantages of the polynucleic system, e.g. ageing and weathering resistance, have been added to the compositions;

(b) the content of hydroxyl groups positively effects the adhesive properties. Thus, a favourable wetting of glass, quartz, sand, stone, etc. and excellent adhesive properties are achieved.

Contrary to processes utilizing cold hardening epoxides, fast hardening of the compositions of the present invention is still possible even at temperatures of e.g. minus 10°C. Whereas the application of cold hardening epoxides is limited to temperatures in excess of 5°C, due to temperature sensitivity, the hardening of the radically hardenable compositions in accordance with the present invention may be effected by means of peroxides in the same manner as unsaturated polyesters.

There is a further advantage that due to an essentially lower volume concentration of ester groups, when compared with unsaturated polyester resins, a high resistance against alkaline soaping is given. An additional advantage is due to the fact that the double bonding, especially at the end of the chain, is specifically reactive since it is not sterically impeded. Contrary to the sterically impeded double bonding inside the polyester chain in the case of unsaturated polyester resins, the compositions in accordance with the invention react quickly and quantitatively with their double bonds. Due to the preferred position of the reactive group in the agents in accordance with the invention, they are able to harden without the addition of reactive thinners or other comonomeres.

When using the compositions in accordance with the invention, a hardened product is obtained due to the wetting abilities, which, compared to the hardened, unsaturated polyester resins, is far more elastic and has an increased cracking resistance. Due to the high elongation and tear the agents are able to absorb, largely tension-free, the volume contractions which occur.

Mixtures with the following mixing ratios, in relation to the total mixture but without hardener, have proved to be of particular advantage:

reactive resin	9 - 28 weight percent
reactive thinner	4 - 16 weight percent
fillers	56 - 82 weight percent

These mixing limits may, for example, be applied with 5% hardening components. Together with the hardener and as a hardening component, phlegmatization agents may be employed, i.e. organic phlegmatization agents, such as phthalates, chloroparaffine, as well as inorganic phlegmatization agents, e.g. gypsum, chalk, silicic acid or water. Such phlegmatization agents are contained in subordinate quantities, e.g. in the range of 0.5 to 3.5 percent by weight of the total mixture, as well as activators which, if they are present, are contained in a range of 0.005 to 2.0 percent by weight of the total mixture.

Of particular advantage is the use of the compositions of the present invention for fastening dowels and anchor rods in drill holes. The reactive resin and the hardener, each with their desirable components, may be introduced in the drill hole either separately or together immediately after mixing them. Mostly, however, the reactive resin and the hardener remain separated for this purpose in a unit, e.g. in a cartridge. These cartridges or similar units usually consist of glass or a similar, easily destructible material, including e.g. a brittle synthetic material. The cartridge is then destroyed once inserted into the drill hole by rotating the dowel or the anchor rod, whereby the casing of the material may serve as filler and should then be added to the filler proportion. It is, however, also possible to use systems in which one component, e.g. the hardener, is micro-capsuled. When inserting the anchor rod, the wall material of the micro-capsule is destroyed.

The high elongation and tear of the compositions of the present invention guarantees an almost completely tension free absorption of the volume contraction which occurs during hardening. If pressure is exerted on the anchor, a drill hole depth dependent elongation of the anchor rod occurs. When compared with known bonding anchors based on unsaturated polyesters, the elastic compositions in accordance with the invention guarantee a more favourable load distribution over the entire bonding area and especially a decrease in tension peaks on the surface of the absorbent, e.g. concrete. In general, the compositions in accordance with the invention, which contain a mixture of acrylic acid modified bisphenolic compounds and acrylic acid modified Novolak compounds lead to products with a higher thermo-forming resistance which is particularly important for their use in the bonding anchor area for fastening the dowel and anchor rods in drill holes. This is due to a higher degree of wetting which is the result of the molecular structure. This higher resistance to changes in temperature is linked with a higher resistance to chemicals. A further advantage is the increased resistance to weathering and the low water absorption even with long contact with water.

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The compositions in accordance with the invention may contain known reactive resins, such as unsaturated polyester resins, methyl-methacrylate resins or other known epoxy resins in possibly subordinated quantities in the sense of a modification of the properties.

The epoxy-bisphenols, as well as the -Novolaks may be produced, in the usual manner, by a reaction of the bisphenol and/or the Novolak with e.g. epichlorohydrin (viz. e.g. H.G. Elias, Macro-molecules, Basel, Heidelberg 1972, p. 707-709).

The following examples describe the invention in detail.

Example 1

Bisphenol-A-methacrylate (MW: 492-775)	17.90 weight percent
Novolak methacrylate (MW: 780-1200)	4.3 weight percent
Monostyrol	12.20 weight percent
Divinyl benzol	1.00 weight percent
Quartz sand 0.1....0.25 mm	30.00 weight percent
Quartz sand 0.3... 0.65 mm	30.10 weight percent
Dimethyl-p-toluidin	0.05 weight percent
Dibenzoyl peroxide (50 % in chloro paraffine)	4.45 weight percent
	100.00 weight percent

By mixing, a material with a filling consistency is obtained.

Gelling time	3 - 3.5 minutes
Hardening time	35 minutes
Strength	
Anchor rod	M12
Insertion depth	110 mm
Drill hole diameter	14 mm
Concrete: B 35, actual strength $48 N/mm^2$	
Break value	74 kN

Example 2 dimension M 12

a) outer cartridge

glass weight	5.6 g
glass outside diameter	10.75 mm
glass wall thickness	0.55 mm
cartridge length	100 mm
bisphenol-A-methacrylate (65% in monostyrol, amine accelerated)	4.3 g
quartz (grain size 1,5-2,0 mm)	6.6 g

b) inner cartridge

glass weight	1.2 g
glass outside diameter	6.30 mm
glass wall thickness	0.65 mm
cartridge length	80 mm
dibenzoyl peroxide (20% in gypsum)	0.8 g

Example 3

a) outer cartridge

glass weight	5.8 g
glass outside diameter	9.20 mm
glass wall thickness	0.45 mm
cartridge length	90 mm
bisphenol-A-acrylate (55% in monostyrol, 40 parts, divinylbenzol 5 parts, accelerated with 0,15% dimethyl-p toluidin)	3.8 g

b) inner cartridge

glass weight	2.2 g
glass outside diameter	10.75 mm
glass wall thickness	0.45 mm
cartridge length	90 mm
quartz (1,2 - 1,8 mm)	5.4 g
dibenzoyl peroxide (50% in phtalate)	0.8 g

Example 4

a) outer cartridge

glass weight	5.8 g
glass outside diameter	10.75 mm
glass wall thickness	0.45 mm
cartridge length	110 mm
bisphenol-A-methacrylic acid-ester, pre-accelerated with amine)	4.2 g

b) inner cartridge

glass weight	2.2 g
glass outside diameter	9.20 mm
glass wall thickness	0.45 mm
cartridge length	90 mm
quartz (o,04 - 0,15 mm)	0.4 g
quartz (1,2 - 1,8 mm)	5.0 g
dibenzoyl peroxide (50% in chalk)	0.5 g

Example 5

a) outer cartridge

glass weight	5.6 g
glass outside diameter	10.75 mm
glass wall thickness	0.45 mm
cartridge length	100 mm
bisphenol-A-methacrylate MW: 492 - 775 (75% in monostyrol)	3.0 g
Novolak methacrylate MW: 780 - 1200 (60% in monostyrol)	1.2 g
cobalt octoate	0.001 g
dimethyl anilin	0.004 g

b) inner cartridge

glass weight	0.7 g
glass outside diameter	43 mm
glass wall thickness	0.65 mm
cartridge length	80 mm
methylethylketon- peroxide	0.35 g

Figures 1 and 2 illustrate, as examples, the reaction products which are contained in the compositions in accordance with the invention. Examples shown refer to preferred forms. The sequence for the formation of the reaction products is diagrammatically depicted, as an example, in Figure 3.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. An acrylate based radically hardenable adhesive, bonding and sealing composition comprising a hardenable acrylate being the reaction product of a first reactant and a second reactant, said first reactant being acrylic acid or an acrylic acid derivative and said second reactant being bisphenol, a Novolak compound containing an epoxy group, or a combination thereof.

2. A composition according to claim 1 wherein the bisphenol compound is bisphenol A, bisphenol F, or a combination thereof.

3. A composition according to claim 1 or 2 wherein the acrylic acid derivative is methacrylic acid, acrylic acid and methacrylic acid amide, halogenide, ester, or a combination thereof.

4. A composition according to any one of the preceding claims wherein the reaction product is formed by the reaction of an acrylic acid derivative with a bisphenol having two epoxy groups, a Novolak compound containing one epoxy group per phenol nucleus, or a combination thereof.

5. A composition according to any one of the preceding claims wherein the reaction product is formed by the reaction of an acrylic acid derivative with either bisphenol, Novolak, or a combination thereof wherein said bisphenol or Novolak compound has been etherized with epoxy groups.

6. A composition according to claim 5 wherein the bisphenol or Novolak compound has been etherized with the phenolic OH groups of the compound.

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7. A composition according to any one of the preceding claims wherein the reaction product is formed by the reaction of an acrylic acid derivative with a bisphenol compound, a Novolak compound, or a combination thereof wherein said bisphenol or Novolak compound contains an alkyl-epoxy group having 3 to 4 carbon atoms.

8. A composition according to any one of the preceding claims wherein the reaction product is formed by the reaction of an acrylic acid derivative and either a bisphenol compound, a Novolak compound, or a combination thereof wherein said bisphenol or Novolak compound contains an epoxy group in the end position.

9. A composition according to any one of the preceding claims comprising from 9 to 28% by weight reactive resin, 4 to 16% by weight reactive thinner and 56 to 82% by weight filler.

10. Use of the compositions according to any one of the preceding claims, for fastening dowels and anchor rods in drill holes.

11. A composition substantially as herein before described with reference to any one of the examples.

DATED this 15th day of JUNE, 1989

HILTI AKTIENGESELLSCHAFT

Attorney: PETER HEATHCOTE

Fellow Institute of Patent Attorneys of Australia

of SHELSTON WATERS

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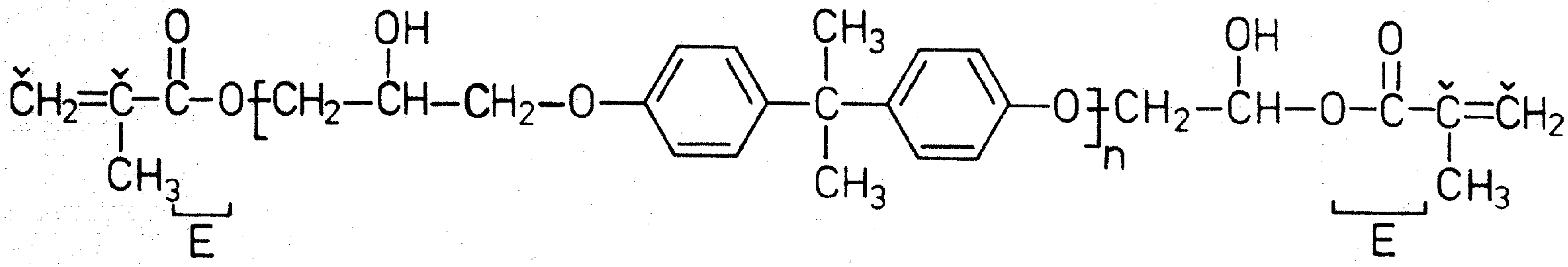

BISPHENOL - A - METHYLMETHACRYLATE

n = 1 ÷ 2

Fig. 1

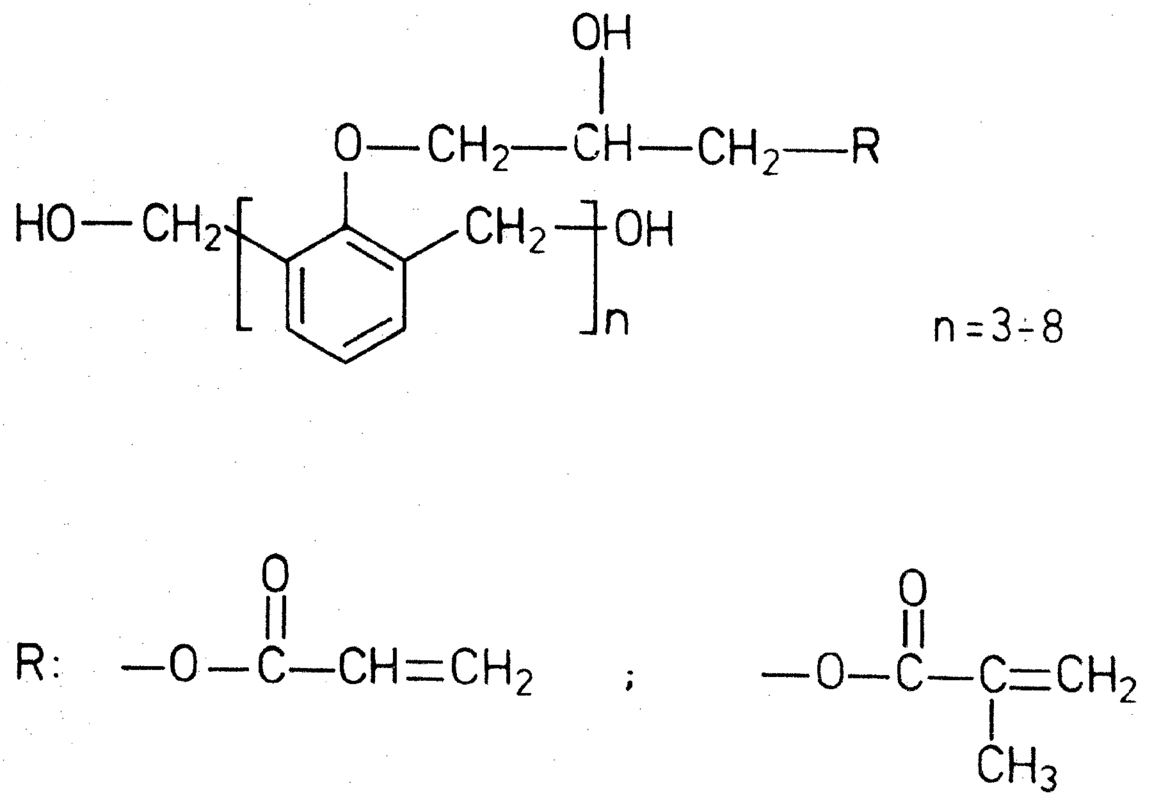

Fig. 2 STRUCTURE OF A NOVOLAK EPOXY ACRYLATE

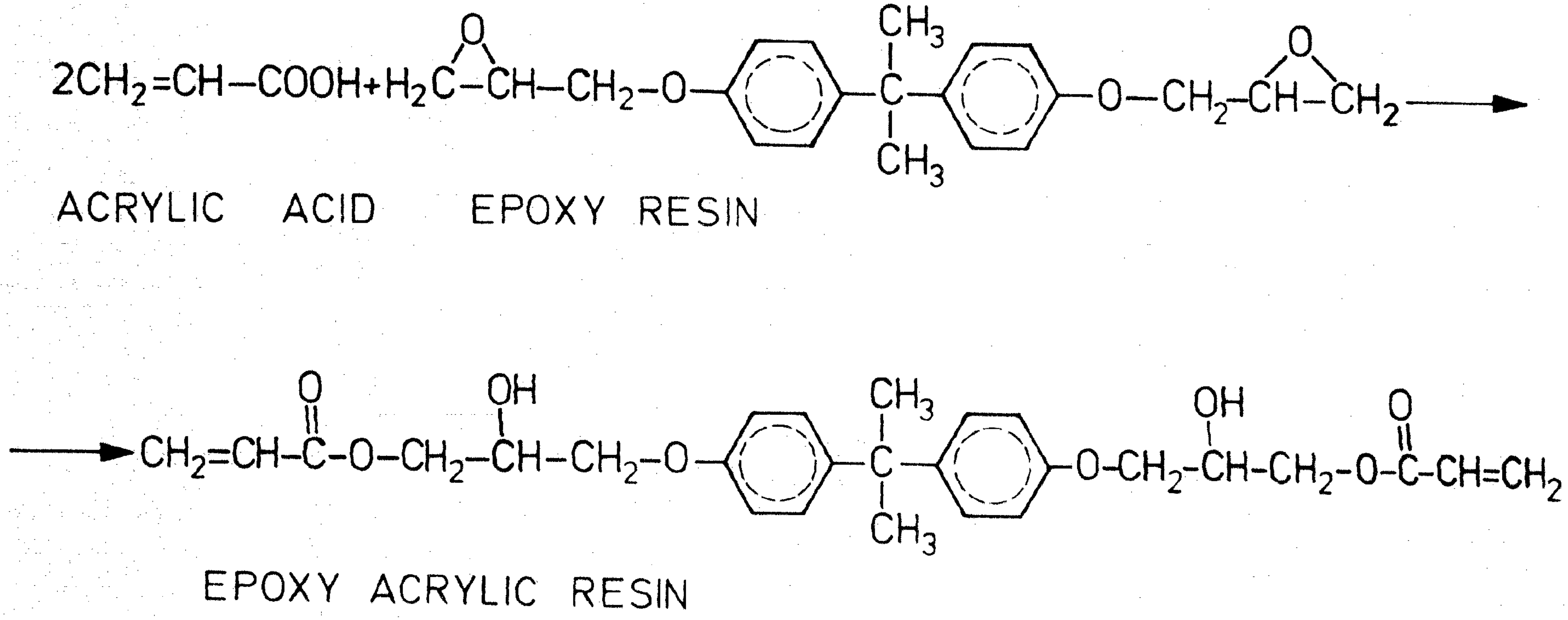

Fig. 3